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(19)

(54) BLEACHING COMPOSITIONS

(71) We, THE PROCTER & GAMBLE COMPANY, a Company organised under the laws of the State of Ohio, United States of America of 301 East Sixth Street, Cincinnati, Ohio 45202, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be paricularly described in and by the following statement:—

The present invention relates to bleaching compositions comprising two types of granular particles. In one granule type, peroxyacid bleaching agents are admixed with stabilizing agents and water of hydration and then uniformly coated with a fatty alcohol material to delay bleaching granule solubility. Such bleaching granules are admixed with agglomerated granules of a suitable buffering agent which are likewise only slowly soluble in aqueous solution. Utilization of such two-granule bleaching compositions provides aqueous bleaching solutions having proper concentrations of peroxyacid bleaching agents and proper pH conditions for effective bleaching of colored fabrics without the usual attendant fabric color damage.

It is well recognized that peroxygen bleaching agents are highly useful for chemical bleaching of colored fabrics and textiles inasmuch as such bleaching agents are generally less harsh and more suited for colored fabric bleaching than conventional bleaching agents of the active chlorine type. Such peroxygen bleaching products have generally been solid or granular in nature owing to the difficulty of preserving the active oxygen content of liquid peroxygen systems.

Utilization of such granular peroxygen bleaching products is not, however, without its difficulties insofar as fabric color damage is concerned. Such products are generally added to a dry load of laundry in a conventional washing machine and dry bleach remains in close contact with fabrics during the time that such conventional washing machines are being filled with hot water. As the washing machine tub fills, local high concentrations or even pastes of peroxygen bleaching product come into contact with fabric surfaces. When this happens, highly effective bleaching conditions exist at very small spots or "pinpoints" on fabric surfaces, and such conditions can result in damage to fabric color in such a "pinpoint" pattern.

"Pinpoint" color damage can be minimized somewhat by employing methods to delay solubility of the bleaching material until after the washing machine tub has completely filled and agitation has begun to disperse local areas of high bleach concentration. One such method has been to coat or encapsulate bleaching granules with a material that prevents immediate contact of water and bleaching agent upon addition of the dry bleach product to water.

Such coating procedures are not, however, without difficulties. A coating material must be employed which adequately serves to delay bleach introduction into aqueous bleaching solution for a sufficient amount of time at conventional wash water temperatures. At the same time, the coating must be of a nature that will allow complete release of peroxygen bleach into solution later in the wash cycle. Furthermore, such coating material must be sufficiently soluble so as not to deposit in an unsightly manner on fabrics being bleached and laundered. Additionally, an appropriate coating material must also aid in stabilization of the chemically reactive bleaching agents during prolonged periods of storage of the concentrated granular bleaching product. Finally, such coating must not itself react with other alkaline bleach composition additives.

Even if, however, such troublesome bleach coating problems can be overcome, some "pinpoint" color damage can still result upon dissolution of the coating and release of the bleaching agent into solution. Such pinpoint color damage occurs because even after delayed release, bleaching concentrations can be sufficiently high in localized areas to cause fabric

color damage under the influence of the relatively alkaline pH conditions of conventional fabric laundering. It is at such pH conditions of from about 7 to 9 that peroxygen bleaching agents are of sufficient solubility and effectiveness to cause this "pinpoint" color damage. Thus the problem of "pinpoint" color damage is a complex one for which no simple solution has heretofore been discovered.

It has been surprisingly discovered that by combining fatty alcohol coated bleaching granules containing particular peroxyacid bleaching agents and particular bleach stabilizing materials, with certain pH adjustment granules having particular buffering and solubility characteristics, bleaching compositions can be formulated which are surprisingly superior to similar bleaching compositions of the prior art. In particular, compositions can be formulated that can be effectively utilized as bleaching agents for colored fabrics, that minimize the "pinppoint" fabric color damage usually associated with use of solid peroxygen bleaching products, that are in convenient "commercially acceptable" granular form and that have sufficient chemical storage stability to be useful after prolonged periods of storage. Furthermore, methods are provided for utilizing the particularly desirable bleaching agents of the peroxyacid type under conditions of conventional home laundering operations for effective but safe chemical cleaning of colored fabrics and textiles.

The present invention provides a bleaching composition comprising

(A) from 1% to 50% by weight of bleaching granules comprising
  (i) from 1% to 40% by weight of said bleaching granules of a normally solid, organic, water-soluble peroxyacid or a water soluble salt thereof;
  (ii) from 5% to 45% by weight of said bleaching granules of a water-soluble bleach-stabilizing agent selected from alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of an acid having an ionization constant at 25°C for the first hydrogen of at least 1×10^{-3};
  (iii) from 5% to 45% by weight of said bleaching granules of water of hydration; and
  (iv) from 3% to 35% by weight of said bleaching granules of a fatty alcohol coating material, said coating material having a melting point within the range of 95°F to 105°F; said coating material further encapsulating said peroxygen compound, stabilizing agent and water of hydration in a substantially uniform manner; and

(B) from 50% to 99% by weight of alkaline pH-adjustment granules comprising an alkaline water-soluble buffering agent capable of yielding an aqueous solution pH of from 7 to 9, the buffering agent being agglomerated with an agglomerating agent in a manner such that no more than 50% of said buffering agent dissolves within the first four minutes after introduction of the alkaline pH-adjustment granules into an unagitated aqueous medium of a temperature of 110°F or less and such that substantially all of said buffering agent dissolves within the first 7 minutes after introduction into an aqueous medium (by which there is meant the contents of automatic laundering apparatus under conventional laundering conditions) of a temperature of 110°F or greater under conditions of home laundering agitation.

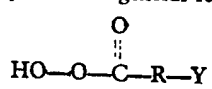
The present bleaching compositions are especially adapted to minimize "pinpoint" fabric color damage and, as stated, comprise two essential granular components, *viz* bleaching granules and alkaline pH-adjustment granules. The nature of these two essential components as well as optional components and composition formulation and use are discussed in detail as follows.

Bleaching Granules.

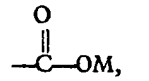
From 1% to 50% by weight, preferably from 10% to 30%, especially 20% to 30% by weight of the present bleaching compositions comprise bleaching granules having particular essential characteristics. Such bleaching granules themselves consist essentially of four components: a peroxyacid compound, a stabilizing agent, water of hydration and a fatty alcohol coating. Optional materials can also be present within such bleaching granules.

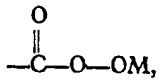
Peroxyacid Compound.

The bleaching granules of the present invention comprise from 1% to 40%, preferably from 25% to 40% by weight of the bleaching granules of a normally solid, water-soluble peroxyacid compound. A compound is "normally solid" if it is in dry or solid form at room temperature. Suitable peroxyacid compounds are the organic peroxyacids and water-soluble salts thereof which in aqueous solution yield a species containing a —O—O moiety. These materials may have the general formula



wherein R is an alkylene group containing from 1 to 16 carbon atoms or an arylene group containing from 6 to 8 carbon atoms and Y is hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous soultion. Such Y groups can include, for example,





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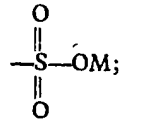
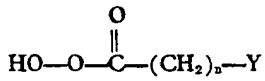
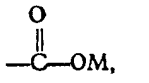


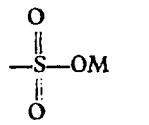
wherein M is H or a water-soluble salt-forming cation.

The organic peroxyacids and salts thereof, for use in the compositions of the present invention, can contain either one or two peroxy groups and can be either aliphatic or aromatic. When the organic peroxyacid is aliphatic, the unsubstituted acid may have the general formula



where Y, for example, can be CH_3, CH_2Cl,





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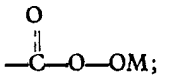
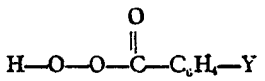
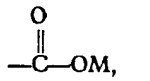


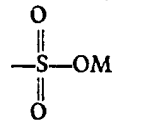
and n can be an integer from 1 to 12. Perazelaic acids (n=7) are the preferred compounds of this type. The alkylene linkage and/or Y (if alkyl) can contain halogen or other non-interfering substituents. Examples of preferred aliphatic peroxyacids are diperazelaic acid and diperadipic acid.

When the organic peroxyacid is aromatic, the unsubstituted acid may have the general formula



wherein Y is, for example, hydrogen, halogen, alkyl,





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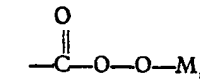

The percarboxy and Y groupings can be in any relative position around the aromatic ring. The ring and/or Y group (if alkyl) can contain any non-interfering substituents such as halogen groups. Examples of suitable aromatic peroxyacids and salts thereof are monoperoxyphthalic acid, diperoxyterephthalic acid, 4-chlorodiperoxyphthalic acid, the monosodium salt of diperoxyterephthalic acid, *m*-chloroperoxybenzoic acid, *p*-nitroperoxybenzoic acid, and diperoxyisophthalic acid.

Of all the above-described organic peroxyacid compounds, the most preferred for use in the present compositions are diperisophthalic acid and diperazelaic acid.

Stabilizing Agent.

From 5% to 45%, preferably from 25% to 40% by weight of the bleaching granules comprises a water-soluble bleach stabilizing agent selected from alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of an acid having an ionization constant at 25°C, for the first hydrogen, of at least 1×10^{-3}. Although, as will be discussed below, the function of such salts is to provide a vehicle for inclusion in the present bleaching granules of water of hydration, the concentration of such materials as specified above is on an anhydrous basis.

In general, the above-described salts include the alkali metal, alkaline earth metal, ammonium, and substituted ammonium sulfates, bisulfates, nitrates, phosphates, pyrophosphates, polyphosphates and hexametaphosphates. Specific examples of such materials include magnesium sulfate, sodium sulfate, potassium sulfate, ammonium sulfate, lithium sulfate, dimethylammonium sulfate, sodium bisulfate, potassium bisulfate, ammonium bisulfate, sodium nitrate, magnesium nitrate, calcium nitrate, sodium tripolyphosphate, trisodium phosphate, sodium metaphosphate, sodium hexametaphosphate, potassium pyrophosphate, and sodium tetraphosphate. Stabilizing agents of this type are described more fully in U.S. Patent 3,639,285.

Of all the above described stabilizing agents,

the preferred salts are sodium tripolyphosphate and magnesium sulfate. Another preferred stabilizing agent is disoclosed in British Patent Apolication No. 21239/74, Serial No. 1,456,591 in which there is claimed a stable, phosphate-free, granular bleaching composition comprising (A) from 1% to 40% by weight of a normally solid water-soluble peroxyacid component selected from organic peroxy acids and salts thereof; (B) from 1.5% to 45% by weight of a stabilizing-agent mixture consisting of: (i) magnesium sulfate; and (ii) an alkali metal sulfate selected from sodium sulfate, and potassium sulfate and mixtures thereof; the weight ratio, on an anhydrous basis, of magnesium sulfate to alkali metal sulfate being from 60:1 to 6:1, and (C) from 5% to 45% by weight of water of hydration; the weight ratio of magnesium sulfate to peroxyacid compound being 1.5:1 or less. In a highly preferred embodiment, the bleaching granules contain from 25% to 40% by weight of magnesium sulfate and from 1% to 3% by weight of sodium sulfate.

Water of Hydration.

From 5% to 45%, preferably from 25% to 40% by weight of the bleaching granules comprises water of hydration. Such water of hydration seves to stabilize the above-described peroxyacid bleaching agents against chemical decomposition. Water of hydration is, of course, chemically bound to the above-described bleach stabilizing salts.

Coating Material.

From 3% to 35%, preferably from 10% to 25% by weight of the bleaching granules comprises a suitable fatty alcohol coating material. The fatty alcohol coating material encapsulating the bleaching granules of the present compositions serves to delay solubility of the peroxyacid bleaching agent upon contact of said granules with water. Such solubility delay of appropriate duration in combination with bleaching solution pH adjustment provided by the alkaline pH adjustment granules described hereinafter serves to surprisingly minimize "pinpoint" fabric color damage normally encountered with the use of peroxyacid bleaching agents.

Utilization of a bleaching granule coating material ensures that local high bleaching agent concentrations are never reached at a point in time when such concentrations could bring about "pinpoint" fabric color damage. The bleaching granule coating material also serves to help stabilize the active bleaching agents against chemical decomposition and loss of bleaching activity during storage.

While the coating material of the bleaching granules must, as described above, be suitable to appropriately delay dissolution of the contents of the bleaching granule, the particular coating material employed also must, after a suitable period of time, be capable of completely releasing into aqueous solution enough active bleaching agent to perform the desired bleaching function. Furthermore, the coating material (after yielding the bleaching granule contents) must be sufficiently water-soluble or dispersible so that it does not deposit in an unsightly manner on the fabrics or textiles being bleached. Finally, the coating material must not react with other alkaline ingredients of the granuular bleaching composition during storage of the concentrated product. (Some common coating materials of the prior art, such as fatty acids, tend to saponify under such conditions and are hence undesirable.)

The two factors which determine whether any bleaching granule coating material will perform its intended function in a commercially acceptable bleaching composition are 1) the type of coating material employed and 2) the melting point of the coating material. It has been surprisingly discovered that for utilization in the particular bleaching compositions of the present invention, such coating material must be 1) a fatty alcohol, having 2) a melting point within the range of from 95°F. to 105°F. Preferably such fatty alcohol coating has a melting point within the range of from 95° to 100°F.

A most preferred fatty alcohol coating material, which does have melting point characteristics falling within the above described range is substantially pure myristyl (C_{14}) fatty alcohol. Other fatty alcohol coating materials can be employed as mixtures having the requisite melting point characteristics. Such mixtures can comprise saturated and unsaturated fatty alcohols containing from about 10 to 18 carbon atoms. Conventional melting point determination techniques can be employed by the skilled artisan to formulate a wide variety of such fatty alcohol mixtures having the requisite characteristics described above.

In order to be effective to appropriately delay solubility of the bleaching granule materials, the fatty alcohol coating of said granules encapsulates the peroxyacid compound, stabilizing agent and water of hydration in a substantially uniform manner. Thus, the thickness of the fatty alcohol coating must remain substantially constant. Generally such coating thickness can vary between about 50 and 500 microns.

Coating of the above described bleaching granules in a substantially uniform manner is accomplished by introducing a spray of coating material into a rotating drum containing particles or granules containing bleaching agent, stabilizing agent and water of hydration. Any suitable solvent for the coating material can be employed, if desired, to enhance the ease of spraying such coating material onto the bleaching granules.

Optional Bleaching Granule Components.

In addition to the above-described essential bleaching agent, stabilizing agent, water of hydration, and coating, the above described bleaching granules can optionally contain within the coating material other ingredients designed to improve performance of the present bleaching compositions under special circumstances. Such optional bleaching granule components can include, for example, bleach activators, acidic, pH adjustment agents, dyes and coloring materials.

The most commonly employed optional bleaching granule component is an acidic pH adjustment agent. Generally the amount of peroxyacid bleaching material, when employed in combination with the requisite amount of agglomerated alkaline buffering agent described below, is such that overall bleaching solution pH will fall within an appropriate range for optimal fabric bleaching. Occasionally, however, the present bleaching compositions may be used under conditions such that dissolution of the essential ingredients will not provide a bleaching solution pH within the desired range. Such a situation can occur, for example, if the present bleaching compositions are employed in conjunction with conventional detergent compositions which yield an exceptionally high pH in aqueous solution. In that instance, more acidic material than is essentially present as peroxyacid in the bleaching granuules may be required, and an additional acidic pH adjustment can be incorporated.

Optional pH adjustment agents are those "normally solid" organic or inorganic acids, acid mixtures or acid salts which are in dry or solid form at room temperature. Examples of such suitable pH adjustment agents include citric acid, glycolic acid, tartaric acid, maleic acid, gluconic acid, boric acid, glutamic acid, isophthalic acid, sulfamic acid and mixtures of citric acid and lauric acid. A highly preferred pH adjustment agent by virtue of its relatively low toxicity is citric acid.

If employed, the optional solid acidic pH adjustment agent can comprise from 1% to 20% by weight of the bleaching granules.

Other optional bleaching granule components such as bleach activators, dyes and coloring agents merely represent conventional, well known bleaching composition additives. If present, such other optional materials generally comprise no more than 5% by weight of the total bleaching granules.

Alkaline pH Adjustment Agent.

The second essential component of the bleching compositions of the present invention comprises akaline pH adjustment granules. Such pH adjustment granules generally constitute from 50% to 99% by weight of the total composition, preferably from 60% to about 90% by weight. These essential granules comprise an agglomerated alklaine water-soluble buffering agent capable of yielding an aqueous solution pH of from 7 to 9.

Particular inorganic salts or mixtures thereof are employed to realize buffering agents having the particular pH maintenance capability desired. Such salts can include, for example, certain phosphates, carbonates and bicarbonates and mixtures thereof. A highly preferred buffering agent for use in the pH adjustment granules of the present invention is sodium bicarbonate which buffers in the pH range of from 8 to 8.5.

It has been discovered that as with the peroxyacid bleaching agent, it is essential that solubility of the necessary buffering agent be delayed for a period of time after first contact of the present bleaching compositions with water. Peroxyacid water solubility is dependent upon pH, with the peroxyacids generally being more water-soluble within the alkaline pH range. Delayed solubility of the buffering agent and the resultant delay in attainment of alkaline pH conditions within bleaching solution thus serves to inhibit formation of locally high concentrations of peracid. Furthermore, such delayed solubility of the buffering agent ensures that during initial contact with water, the peracid which does dissolve is not present under pH conditions conducive to color destroying activity of the bleach. It is only after washing machine agitation has begun and the local areas of relatively heavy bleaching gent concentrations have been dissipated that the buffering agent dissolves and is able to maintain overall bleaching solution pH within the desired range for optimum fabric bleaching.

Solubility of the buffering agent is delayed in the context of the present invention by means of agglomerating the normally solid buffering agent material into granules by means of an agglomerating agent. Agglomeration is a well known granule formation technique and can be undertaken in any convenient, conventional manner. Generally, an aqueous slurry or melt of an agglomerating medium is prepared and sprayed into an agitated dry mixture of the powdered buffering agent. Any suitable spraying device can be used to spray a mixture of water and the agglomerating medium or melted agglomerating medium onto the dry mixture of the buffering agent.

A wide variety of agglomerating media can be employed. Agglomerating media include any moderately water-soluble or dispersible adhesive material such as sodium or potassium silicate, animal and synthetic resin glues, polymers such as polyoxyethylene and polyvinylalcohol, fatty acids, fatty esters, polysaccharides such as dextrin, and waxes.

The particular agglomerating medium and/or procedure employed is not critical so long as granular particles of buffering agents are prepared which exhibit the effect of delayed or impeded solubility of the alkaline buffering

agent upon contact with water. We are here concerned with such water contact as will take place under conditions of conventional fabric laundering operations in automatic laundering apparatus. Under such conditions, water is present in the washing machine tub for about four minutes while the tub is filling with water. Thereafter, agitation begins by means of a rotating agitator device mounted within the tub of the automatic washing machine.

The alkaline pH adjustment granules of the present invention are agglomerated in a manner such that no more than 50% of the buffering agent present dissolves within the first four minutes after introduction of the agglomerated buffering agent granules into an unagitated aqueous medium having a temperature of 110°F or less. The agglomerated alkaline pH adjustment agent granules should, however, be essentially completely dissolved within a period of not more than 7 minutes after introduction into aqueous medium at 110°F or greater, said aqueous medium being under conditions of conventional home laundering agitation. Conventional solubility determination techniques can be employed in the synthesis of agglomerated pH adjustment granules having the solubility characteristics described above.

The alkaline pH adjustments granules of the present invention can optionally contain materials other than the above described buffering agent and agglomerating medium. Such granules can, for example, contain perfume, dye, coloring agents or water. If such optional materials are present in the alkaline pH adjustment granules of the present invention, such optional ingredients usually comprise no more than 5% by weight of the pH adjustment granules.

Composition Preparation.

The bleaching compositions of the present invention are prepared by formulating separately each of the two types of granules essentially present and subsequently admixing these two granule types in the appropriate proportion. The bleaching granules themselves are prepared in any conventional manner such as by admixing ingredients, agglomeration, compaction, or granulation. In a preferred method for preparing the bleaching granules of the present compositions, a peroxyacid-water mixture containing from about 35% by weight to about 50%, by weight of water is combined with stabilizing agent and any optional bleaching granule materials (all in appropriate proportions) and thoroughly mixed. Such mixture is then fed through an extruder. Extrudate in the form of noodles is fed into a spheronizer (also known by the tradename, "Marumerizer", which is a registered trade mark) to form approximately spherical particles from the peroxyacid-containing noodles. In the spheronizer the particles can be dried to the extent necessary to provide the requisite water content of the granules. Upon leaving the spheronizer, such particles are screened to provide uniform particle size and are then returned to a rotating drum for coating. Coating is accomplished as described above by introducing into the rotating drum along with the spheres a spray of the fatty alcohol coating material. The agglomerated alkaline pH adjustment granules can be prepared by any conventional agglomeration process as noted above.

The bleaching compositions of the present invention can optionally contain granules of a third type if "specialty" bleaching compositions are desired. For example, it is possible to admix with the essential bleaching granules and pH adjustment granules, granules of conventional spray-dried detergent material. Such optional detergent "third granules" can, of course, contain conventional anionic, nonionic, ampholytic or zwitterionic surfactants which will not be oxidized by the peroxyacid; organic and/or inorganic alkaline builder salts; as well as conventional fillers, suds suppressants, corrosion inhibitors, anti-redeposition agents, brighteners, dyes or perfumes. When employed such surfactant/builder granules generally comprise from about 20% to 95% by weight of the composition.

The present bleaching compositions can also contain as an optional "third granule" component, the same type of acidic pH adjustment agent described above as being optionally useful *within* the coated bleaching granule in admixture with peroxyacid, stabilizing agent and water. Such optional "third-granule" acidic pH adjustment agents can comprise from about 1% to 10% by weight of the composition. As in the case of those "internal" optional pH adjustment agents, the preferred external or "third-granule" acidic pH adjustment agent is citric acid.

Actual particle size of either the essential bleaching and pH adjustment granules or optional third granules of the present compositions is not critical. However, if granular bleaching compositions are to be realized having commercially acceptable flow properties, certain granule size limitations are highly preferred. All granules of the present compositions preferably range in size from 100 microns to 3,500 microns, more preferably from 900 microns to 1,500 microns. Additionally, flowability is enhanced if particles of the present compositions are of approximately the same size. Therefore, preferably the ratio of the average particle sizes of the bleaching granules and pH adjustment granules varies between 0.5:1 and 2.0:1. Likewise the ratio of the average particle sizes of the essential granules and the non-essential third granule types also varies between 0.5:1 and 2.0:1.

Fabric Bleaching Methods.

By utilizing compositions of the present invention dissolved in water, effective bleaching of colored fabrics and textiles can take place. Generally compositions of the present invention are dissolved to the extent of from 0.01% to 0.2% by weight, preferably from 0.08% to 0.12% by weight in order to carry out such fabric bleaching. Such concentrations generally provide in solution enough peroxyacid bleaching agent to yield from 1 ppm to 100 ppm available oxygen in solution.

The bleaching compositions of the present invention are able to minimize "pinpoint" fabric color damage by ensuring that within bleaching solution only certain essential concentrations of peroxyacid bleach under certain essential pH conditions are at all times and locations present. It has been discovered that peroxyacid bleaching agents can be utilized in aqueous solutions at concentrations that provide from 1 ppm to 50 ppm, preferably from 3 ppm to 15 ppm, of available oxygen, within the pH range of from 7 to 9 and provide excellent fabric bleaching without the attendant pinpoint fabric color damage. At such concentrations and pH conditions, overall color damage and fading is also surprisingly minimized.

The bleaching compositions of the present invention are illustrated by the following examples:

EXAMPLE I.

A two-granule dry bleaching composition is formulated as follows:

Bleaching granules of the following composition are prepared:

Component	%Wt.
Diperisophthalic Acid	25.1%
Magnesium Sulfate Stabilizing Agent	32.5%
Water of Hydration	21.5%
Myristyl Alcohol Coating (Melting point 98°F)	20.9%
	100.0%

The myristyl alcohol is sprayed onto the bleaching granules and thereby is present in a substantially uniform coating completely encapsulating the bleaching granules. The average size of the bleaching granules is 1100 microns.

Agglomerated pH adjustment granules of the following composition are prepared:

Component	%Wt.
Sodium Bicarbonate Buffering Agent	86.2%
Dextrin Agglomerating Medium	6.85%
Water	Balance

The pH adjustment granules are agglomerated by introducing a spray of a 33% by weight dextrin aqueous solution into a tumbling drum containing powdered sodium bicarbonate. Agglomeration in this manner produces sodium bicarbonate agglomerates having the above composition, with an average particle size of about 1200 microns. With such granules in this form only about 46% of the sodium bicarbonate introduced into unagitated water at 110°F. dissolves after the first four minutes. Substantially all of the sodium bicarbonate is, however, dissolved after 3 minutes of agitation in a conventional automatic washing machine.

The two granule types are thoroughly admixed to form a uniform granular composition containing 34.88% by weight of the bleaching granules and 65.12% by weight of the pH adjustment granules. Such a composition provides excellent bleaching of colored fabrics with minimal pinpoint fabric color damage when such a composition is dissolved in aqueous bleaching solution in a conventional washing machine at a concentration sufficient to provide about 10 ppm available oxygen. Such a composition further has commercially acceptable storage stability.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when in the Example I composition, the diperisophthalic acid is replaced with an equivalent amount (in terms of available O_2) of diperazelaic acid, diperadipic acid, monoperoxyisophthalic acid, monosodium salt of diperoxyterephthalic acid, p-nitroperoxybenzoic acid, 4-chlorodiperoxyphthalic acid or m-chloroperoxybenzoic acid.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when in the Example I composition, the magnesium sulfate stabilizing agent is replaced with an equivalent amount of sodium sulfate, potassium sulfate, ammonium sulfate, lithium sulfate, dimethylammonium sulfate, sodium bisulfate, potassium bisulfate, ammonium bisulfate, sodium nitrate, magnesium nitrate, calcium nitrate, sodium tripolyphosphate, trisodium phosphate, sodium metaphosphate, sodium hexametaphosphate, potassium pyrophosphate, sodium tetraphosphate or mixtures thereof.

Substantially similar bleaching and color damage performance as well as substantially similar product stabiity are realized when in the pH adjustment agent granules of the Example I composition, the sodium bicarbonate buffering agent is replaced with an equivalent amount of an agglomerated mixture of disodium hydrogen phosphate and sodium dihydrogen phosphate, said pH adjustment agent granules having substantially equivalent solubility characteristics, and providing a sub-

stantially equivalent aqueous solution pH.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when in the agglomerated pH adjustment granules the dextrin agglomerating medium is replaced with lauryl alcohol, polyvinylalcohol or sodium siicate utilized in a manner to provide equivalent buffering agent solubility characteristics.

EXAMPLE II.

A three granule dry bleaching composition is formulated as follows:

Bleaching granules of the following composition are prepared:

Component	%Wt.
Diperisophthalic Acid	23.1%
Magnesium Sulfate	23.2%
Sodium Sulfate	1.89%
Water of Hydration	21.4%
Citric Acid pH adjustment agent	7.4%
Minors and Impurities	2.0%
Myristyl Alcohol Granule Coating	21.0%
	100.00%

The myristyl alcohol is sprayed onto the bleaching granules and thereby is present in a substantially uniform coating completely encapsulating the bleaching granules. The average size of the bleaching granules is about 1100 microns.

Agglomerated pH adjustment granules of the following composition are prepared:

Component	%Wt.
Sodium Bicarbonate Buffering Agent	86.0%
Dextrin Agglomerating Medium	7.0%
Perfume	Trace
Water	7.0%
	100.0%

The pH adjustment granules are agglomerated by introducing perfume and a spray of 20% by weight dextrin aqueous solution into a tumbling drum containing powdered sodium bicarbonate,. Agglomeration in this manner produces perfume-containing sodium bicarbonate agglomerates having the above composition, with an average particle size of about 1100 microns. With such granules in this form only about 46% of the sodium carbonate introduce into unagitated water at 110°F. dissolves after the first four minutes. Substantially all of the sodium bicarbonate is, however, dissolved after 3 minutes of agitation in a conventional automatic washing machine.

The two above-described granules types are thoroughly admixed with a third granule type consisting essentially of solid citric acid of average particle size of about 700 microns. Such admixture provides a uniform granular composition containing 24.3% by weight bleaching granules; 71.4% by weight alkaline pH adjustment granules and 4.3% by weight citric acid granules.

Such a composition provides excellent bleaching of colored fabrics with minimal pinpoint fabric color damage when such a composition is dissolved in aqueous bleaching solution in a conventional automatic washing machine at a concentration sufficient to provide about 10 ppm available oxygen. Such a composition has commercially acceptable storage stability.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when the Example II composition is modified in that the diperisophthalic acid is replaced with an equivalent amount (in terms of available O_2) of diperazelaic acid, diperadipic acid, monoperoxyisophthalic acid, monosodium salt of diperoxyterephthalic acid, p - nitroperoxybenzoic acid, 4 - chlorodiperoxyphthalic acid or m-chloroperoxybenzoic acid.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when the Example II composition is modified in that the magnesium sulfate stabilizing agent is replaced with an equivalent amount of sodium sulfate, potassium sulfate, ammonium sulfate, lithium sulfate, dimethylammonium sulfate, sodium bisulfate, potassium bisulfate, ammonium bisulfate, sodium nitrate, magnesium nitrate, calcium nitrate, sodium tripolyphosphate, trisodium phosphate, sodium metaphosphate, sodium hexametaphosphate, potassium pyrophosphate, and sodium tetraphosphate.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when the Example II composition is modified in that the myristyl alcohol coating material is replaced with a mixture of fatty alcohols containing from 10 to 18 carbon atoms, said mixture having a melting point of about 100°F.

Substantially similar bleaching and color damage performance as well as substantially similar product stability are realized when the Example II composition is modified in that the citric acid pH adjustment agent either within the bleaching granules or the third granules is replaced with an equivalent amount of glycolic acid, tartaric acid, maleic acid, gluconic acid, boric acid, isophthalic acid, glutamic acid, sulfamic acid, sodium bisulfate, potassium bisulfate, ammonium bisulfate, or mixtures of citric acid and lauric acid.

Fabric laundering capability as well as substantially similar bleaching/color damage performance and product stability are obtained if the Example II composition is modified by

the addition of about 90% by weight of synthetic detergent granules consisting essentially of linear alkyl benzene sulfonate having an average of 11.8 carbon atoms in the alkyl group and sodium sulfate filler, the bleaching, pH adjustment and other acid granules remaining in the same relative proportions to each other.

Fabric laundering capability as well as substantially similar bleaching/color damage performance and product stability are obtained if the Example II composition is modified by the addition of about 90% by weight of synthetic detergent granules consisting essentially of linear alkyl benzene sulfonate having an average of 11.8 carbon atoms in the alkyl group, a sodium tripolyphosphate builder and sodium sulfate filler; the bleaching, pH adjustment and citric acid granules remaining in the same relative proportions to each other.

Bleaching Performance Tests.

Bleaching efficiency of the instant composition is evaluated by means of a fabric stain removal test. Standard bundles of soiled laundry and stained test swatches of cotton fabric are washed under conventional conditions in a Kenmore (registered trade mark) upright automatic washing machine. Test swatches contain representative stains, of wine, tea and beef gravy. All loads are washed with a commercially available laundry detergent, Tide, used at a concentration of 1 cup per 17—19 gallons. Some loads are washed with detergent alone, some loads additionally contain a commercial liquid hypochlorite bleaching agent, some loads contain the composition of Example II described above. After washing, the stained fabric test swatches are examined for extent of stain removal by means of a Hunter Color Difference Meter with meter readings adjusted to a scale such that swatches washed with detergent alone rated a stain removal score of 0 while hypochlorite stain removal rated 100.

Typical results of such stain removal evaluation as shown in Table I

TABLE I.

BLEACH EMPLOYED	BLEACH CONCENTRATION	STAIN REMOVAL SCORE
Liquid Hypochlorite	200 ppm Av. Cl_2	100
EXAMPLE II Composition	0.1% wt. (10 ppm Av. O_2)	85
No Bleach (Detergent only)	—	0

The above results demonstrate that compositions of the instant invention provide stain removal performance which compares favorably with that of a commercially available harsh active chlorine bleaching product.

The ability of the bleaching compositions of the instant invention to be used with minimal pinpoint fabric color damage is demonstrated by means of a spot bleaching test. Recommended usage of the test bleaching composition i.e. enough to provide 0.1% by weight in wash solution) are divided into several parts and wrapped in different varieties of dyed test fabric swatches. These fabric-bleach composition packets are then placed at the bottom of a Kenmore upright washing machine. Test swatches are then added with no bleach compound therein. A standard laundry bundle of soiled clothes is added, and the wash cycle is begun. One cup of a commercially available laundry detergent, Tide, is then added to the washing machine. At the end of the cycle, the dyed fabrics are removed and visually evaluated for color removal. Comparisons are made against standard swatches using a scale of 0 to 5; 0 representing no color damage and 5 representing severe color damage. The nature of the bleaching composition tested as well as typical color damage evaluations are provided in Table II.

TABLE II.

BLEACH COMPOSITION	BLEACH CONCENTRATION	COLOR DAMAGE RATING
EXAMPLE II Composition	0.1% wt.	1.6
EXAMPLE II Composition with bleaching granules uncoated	0.1% wt.	3.5—4.0
No bleach (Swatch packets contain Tide)	—	0

The above-described testing demonstrates that even under very severe bleach-fabric contact conditions, pin-point damage is minimized. The beneficial effect of bleach granule coating on color damage minimization is demonstrated by the comparison above of compositions containing coated and uncoated bleaching granules.

WHAT WE CLAIM IS:—

1. A bleaching composition comprising

(A) from 1% to 50% by weight of bleaching granules comprising

(i) from 1% to 40% by weight of said bleaching granules of a normally solid, organic, water-soluble peroxyacid or a water soluble salt thereof;

(ii) from 5% to 45% by weight of said bleaching granules of a water-soluble bleach-stabilizing agent selected from alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of an acid having an ionization constant at 25°C for the first hydrogen of at least 1×10^{-3};

(iii) from 5% to 45% by weight of said bleaching granules of water of hydration; and

(iv) from 3% to 35% by weight of said bleaching granules of a fatty alcohol coating material, said coating material having a melting point within the range of 95°F to 105°F; said coating material further encapsulating said peroxygen compound, stabilizing agent and water of hydration in a substantially uniform manner; and

(B) from 50% to 99% by weight of alkaline pH-adjustment granules comprising an alkaline water-soluble buffering agent capable of yielding an aqueous solution pH of from 7 to 9, the buffering agent being agglomerated with an agglomerating agent in a manner such that no more than 50% of said buffering agent dissolves within the first four minutes after introduction of the alkaline pH-adjustment granules into an unagitated aqueous medium of a temperature of 110°F or less and such that substantially all of said buffering agent dissolves within the first 7 minutes after introduction into an aqueous medium of a temperature of 110°F or greater under conditions of home laundering agitation.

2. A composition according to claim 1 wherein the bleaching granules (A) constitute from 10% to 30% by weight of the composition and the alkaline pH adjustment granules (B) constitute from 60% to 90% by weight of the composition.

3. A composition according to claim 1 or 2 wherein the peroxyacid bleaching agent constitutes from about 25% to 40% by weight of the bleaching granules; the stabilizing agent constitutes from 25% to 40% by weight of the bleaching granules; the water of hydration constitutes from 25% to 40% by weight of the bleaching granules; and the fatty alcohol coating material constitutes from 10% to 25% by weight of the bleaching granules.

4. A composition according to claim 1, 2 or 3 wherein the peroxyacid bleaching agent is diperisophthalic acid or diperazelaic acid.

5. A composition according to any one of claims 1 to 4, wherein the stabilizing agent is sodium tripolyphosphate or magnesium sulfate.

6. A composition according to any one of claims 1 to 4, wherein the stabilizing agent is a mixture of magnesium sulfate and sodium sulfate such that the magnesium sulfate constitutes from 25% to 40% by weight of the bleaching granules and the sodium sulfate constitutes from 1% to 3% by weight of the bleaching granules.

7. A composition according to any one of claims 1 to 6, wherein the fatty alcohol coating material is myristyl alcohol.

8. A composition according to any one of claims 1 to 7 wherein the buffering agent in component (B) is sodium bicarbonate.

9. A composition according to any one of claims 1 to 8 wherein the bleaching granules additionally contain from 1% to 20% by weight of said granules of an acidic pH adjustment agent selected from citric acid, glycolic acid, tartaric acid, maleic acid, gluconic acid, boric acid, glutamic acid, isophthalic acid, sulfonic acid, sulfamic acid, and mixtures of citric acid and lauric acid.

10. A composition according to any of claims 1 to 9, which contains from 1% to 10% by weight of the composition, of granules of an acidic pH adjustment agent.

11. A composition according to claim 9 or 10 wherein the acidic pH adjustment agent is citric acid.

12. A composition according to any one of claims 1 to 11, wherein the bleaching granules and alkaline pH adjustment granules range in size from 100 microns to 3500 microns.

13. A composition according to claim 12 wherein the bleaching granules and alkaline pH adjustment granules range in size from 900 to 1500 microns and the ratio of the average particle sizes of the bleaching granules and pH adjustment granules is between 0.5:1 and 2.0:1.

14. A composition according to any one of claims 1 to 13, which additionally contains from 20% to 95% by weight of granules containing a surfactant selected from anionic, nonionic, ampholytic and zwitterionic surfactants, and an organic or inorganic alkaline builder salt.

15. A bleaching composition substantially as hereinbefore described in Example I or II.

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